RAMJET TECHNOLOGY

Chapter 18
COMBUSTION PRINC

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TABLE OF CONTENTS

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18.1 FOREWORD

Inquiry into the nature of combustion dates back to the beginning of chemistry itself, and throughout the history of that science the phenomena associated with burning have continually aroused the curiosity of investigators. As a consequence, the literature on the subject is voluminous and is growing at an accelerated rate. For example, the Third International Combustion Symposium, held in Madison, Wisconsin, in September 1948, gave rise to a collection [37] of one hundred original papers, and an even greater number was presented at the Fourth Symposium in Cambridge, Massachusetts, in September 1952. Selection of material for a review is not easy in view of the breadth of current research activity in the field of combustion. An attempt to cover the field with any degree of completeness would have resulted in a mere listing of problems by title; an exhaustive treatment would have essentially limited the discussion to one narrow facet of the field.

Current interest in combustion stems from two sources. First, the phenomena challenge our ability to combine modern knowledge of diverse special fields of physics and chemistry.

The understanding of a flame, for example, requires contributions from thermodynamics, statistical mechanics, fluid dynamics, spectroscopy, and chemical kinetics. Second, practical interest is stimulated by the increasing importance of high-performance engines in aviation and by the fact that over ninety per cent of petroleum products find their application through combustion.

The use of petroleum products as an energy source is approximately equal in amount to that of coal, and the combustion of these two types of fuel represents man's largest chemical operation. It seems, however, that the significance of petroleum products to civilization lies less in the prodigality of their application than in the present uniqueness of their role in providing the motive power for the engines of modern high-speed transportation.

The premiums in motor design are high on fuel efficiency and light, compact packaging. Thermodynamics provides knowledge of the amount of energy that one may expect to obtain from a given fuel. For some purposes special high-energy fuels are required, and much research is devoted to their study. In the majority of cases, however, it is not the thermodynamic potential of the fuel which limits the performance of engines but rather the inability to use this potential to full advantage under the requirements of practical operation. The rate of heat release per unit volume and the stability of the combustion process are generally the limiting factors. One of the principal virtues of a jet engine is its small size and weight. The smallness is limited by the ability to achieve high rates of heat release per unit volume. Knowledge which would give clues to methods of attaining these higher rates, or would set limits on their attainability, would be very desirable. Thermodynamics does not provide such limits. Detailed knowledge of the combustion process itself

will be necessary to establish them. The familiar example of "knock" in the Otto engine indicates that combustion instability may also be a limiting factor in performance.

One recognizes that the designer of combustion chambers is plagued by such things as deposits, erosion, and overheating. These problems, important as they are, will not be discussed here. To the extent that they are peculiar to combustion, their elucidation will come largely from understanding the process of combustion itself. The object of this chapter is to define the subjects of flame propagation and flame stability based on these considerations.

The literature is extensive, even in the field covered by this chapter. The object is not to provide a survey but rather to illuminate the subject and bring out points which may stimulate interest and further thought.

18.2 FLAME PROPAGATION

Theory

It is often true that intuitive familiarity with a phenomenon unconsciously passes for understanding, and the phenomenon of flame propagation is probably no exception. Since almost all chemical reactions are speeded up by an increase in temperature, it does not seem strange that a hot match applied to a stream of combustible gas initiates a vigorous chemical reaction. Nor does it seem strange, since the reactions involved are generally highly exothermic, that the process then proceeds steadily, for it is clear that more than enough heat is liberated to bring the oncoming fresh gases to a high temperature and thus provide a continuous process of ignition. The familiarity of the phenomenon and the plausibility of the reasoning make this simple picture attractive. Unfortunately, there remains a question as to the size of the element of truth in it.

This description of flame propagation outlines (somewhat glibly) the basic concept in a class of flame theories generally referred to as "thermal theories." The early theories were predominantly of this class as are a number of the current ones. Thermal theories recognize the existence of the large temperature gradient across the flame-reaction zone between the cool unburnt gases and the hot burnt gases and emphasize the resulting conduction (transport) of heat in the direction opposite to the flow of the gases. To this heat conduction is ascribed a controlling influence on the flame speed, that is, the velocity of propagation of the flame surface normal to itself into the unburnt gas.

Along with the steep temperature gradients across a
flame front there also must be steep concentration gradients,
for on one side exists one set of molecular species, the re-
actants, and on the other, the products of the combustion pro-
cess. As temperature gradients bring about transport of heat
so must these concentration gradients bring about the trans-
port of matter, the reactants diffusing forward and the products
backward. From the purely thermal viewpoint, this intermixing
of the reactants and products by diffusion would be expected to
have a deleterious effect on the propagation of the flame be-
cause of the dilution of reactants in the zone of reaction.
However, other effects must be considered. The majority of the
chemical processes involved in gas-phase combustion are believed
to proceed through free radical chain reactions. In such reac-
tions the build-up of an adequate concentration of chain-carrying
free radicals is the critical process in initiating a self-
propagating system. In the hot product gases of combustion
there is a large concentration of free radicals in equilibrium
with the more ordinary molecules through the agency of dissocia-
tive processes (e.g., $H_2O \rightleftharpoons H + OH$). The diffusion of these
radicals backward into the unburnt gas might well be an import-
ant factor in the propagation of the flame. Among the free radi-
cals, the hydrogen atom deserves special consideration. Because
of high thermal velocity (low mass) and small size, hydrogen
atoms diffuse much more rapidly than other free radicals. In
1947 Pease and Tanford [33,35,36] obtained a rather good corre-
lation between the burning velocity (flame speed) and the
equilibrium concentration (partial pressure) of hydrogen atoms
in the hot products of moist carbon monoxide-oxygen flames with
nitrogen as a diluent. A number of similar observations have
subsequently been reported by other authors. These results have
led to a class of theories of flame propagation known as "dif-
fusional" theories. In these the controlling role is ascribed

- 5 -

to the diffusion processes rather than to heat transport. An interesting variation in the interpretation of the influence of hydrogen atoms is provided in the suggestion of Bartholome [2], who, noting an apparent generality in the correlation between burning velocity and hydrogen atom concentration, suggests that the action of the hydrogen atoms is not a specific chemical one. Since the recombination of hydrogen atoms releases a large amount of heat, Bartholome would ascribe the efficacy of hydrogen atoms in flame propagation to the heat released by their recombination after diffusion into the unburnt gas. This is essentially a thermal mechanism with the heat transport brought about by diffusional processes.

In addition to the strictly thermal and diffusional theories there are a number of theories which attempt to allow for both processes in one way or another. The differential equations for flame propagation turn out, even in the simplest cases, to defy direct solution. As a result, numerous additional assumptions and approximations are made in order to make the problem tractable. The various theories differ largely in the nature of these approximations and assumptions. Many of the approximations do not lend themselves to an a priori test of their validity, and unfortunately gross correlation with experimental data is generally presented with each theory. The problem of the theory of flame propagation is, in fact, highlighted by the abundance rather than the want of plausible expositions. Further discussion of the details of the various approximate theories would take us well outside the scope of this chapter. An excellent digest of the subject has been prepared by Evans [9]. The approach in the case of Hirschfelder and his colleagues [15, 16] has been to avoid questionable approximations normally made to facilitate the computing and to rely, instead, on modern computing machinery to overcome the mathematical complexity. The

hope is to solve, with realistic rigor, the equations for typical cases, properly including all those processes such as diffusion and heat transport which are known to occur in the flame. Subsequently, it should be possible to sort out from the results the important and the incidental mechanisms. Progress along these lines has been very slow because of numerous difficult problems encountered along the way. The difficulties do not appear to be caused entirely by mere mathematical complexity, but many seem to be related to the fundamentally delicate physico-chemical balance present in a flame. For example, the boundary conditions for the differential equations representing a flame become elusive and require very careful analysis in their formulation. The apparently essential nature of some of these difficulties underlines the importance of such a careful approach for a real understanding of flame propagation and suggests the ephemeral nature of the tablets on which the cruder theories are engraved.

The previous discussion pertains mainly to combustion in premixed gases. There are, of course, other important combustion systems such as diffusion flames and the burning of solids and liquids in air. In these heterogeneous systems, the necessity of the processes of heat transport and diffusion for propagation of the reaction is often more obvious than in premixed systems. For example, in the burning of liquid droplets the requirement of heat transfer to evaporate fuel from the surface and diffusion to mix the fuel with the oxidant seems clear. This does not imply, of course, that the quantitative theory of such systems is simple. In addition to the physical chemistry of the combustion process, there are problems with respect to atomization and particle size, fuel distribution, and droplet evaporation which are peculiar to these systems. Thus the discussion in this chapter is restricted to flames in premixed gases.

Experimental Correlations

The experimental data shed considerable light upon the controversial subject of thermal versus diffusional flame propagation. Although the report by Evans [9] includes more extensive information of this nature, a few selected examples will illustrate the situation.

As has been mentioned earlier, Pease and Tanford found a correlation between the burning velocity and the calculated thermodynamic equilibrium partial pressures of hydrogen atoms in moist carbon monoxide-oxygen flames. Subsequently it was found that the correlation could be improved somewhat by using the sum of the partial pressures of hydrogen atoms and of hydroxyl radicals weighted according to their relative diffusion coefficients. Similar agreement was found also in the case of hydrogen-oxygen flames using nitrogen as a diluent. It was concluded from these results that the diffusion of these radicals was the controlling factor in the flame propagation. If the partial pressure of oxygen atoms had been included on the same basis it would have supplied, in a number of cases, the dominant term. Yet no correlation was found between the flame speed and the partial pressure of oxygen atoms. Tanford and Pease suggest that this is due to the lack of ability of oxygen atoms to contribute significantly to the initiation of carbon monoxide combustion. The contrast between this explanation and Bartholomé's suggestion (mentioned earlier) of a chemically nonspecific nature of the effect of hydrogen atoms is striking.

Subsequent to the publications of Pease and Tanford, Hoare and Linnett [17] re-examined the carbon monoxide flame from the thermal viewpoint. They chose as the significant parameter for correlation a temperature ratio, R, defined as $R = (T_f - T_o)/(T_e - T_o)$, in which T_o is the initial temperature

of the gases, T_f is the flame temperature (i.e., the thermo-
dynamic equilibrium temperature of the hot products), and T_e is
the temperature at which the reaction "becomes thermally uncon-
trolled." The temperature T_e is thus essentially the "ignition
temperature" of the early thermal theories. It should be inter-
preted as the temperature above which the reaction is sufficiently
fast that the heat thus released more than compensates for the
heat lost by dissipative processes. Hoare and Linnett discuss a
means of estimating the dependence of T_e on the initial gas com-
position. Using the same data as Pease and Tanford they plotted
the burning velocity against the parameter R and obtained a cor-
relation of about the same quality as was obtained by Pease and
Tanford with the radical concentration. They conclude, therefore,
that the data do not, on this basis, provide a choice between
thermal conduction and radical diffusion as factors in the propa-
gation of this flame.

Linnett and Hoare [27] have applied the same correlation
tests to the ethylene-oxygen flame with nitrogen and air as
diluents. Their results are given in Figs. 18.2-1 and 18.2-2.
In Fig. 18.2-1 the burning velocity is plotted against the ap-
propriately weighted sum of the radical partial pressures (in
this case, hydrogen atoms, oxygen atoms, and hydroxyl radicals),
and in Fig. 18.2-2 against the temperature ratio parameter, R.
It is evident that there is little to choose between the two
correlations. In commenting on their results the investigators
noted that the non-selectivity arises "because the variation of
the equilibrium concentration of the main diffuser (hydrogen
atoms) follows so closely the variation of the equilibrium flame
temperature." This is, of course, not surprising since the
thermodynamics of the situation requires the dissociative reac-
tions responsible for the production of the atoms to be favored
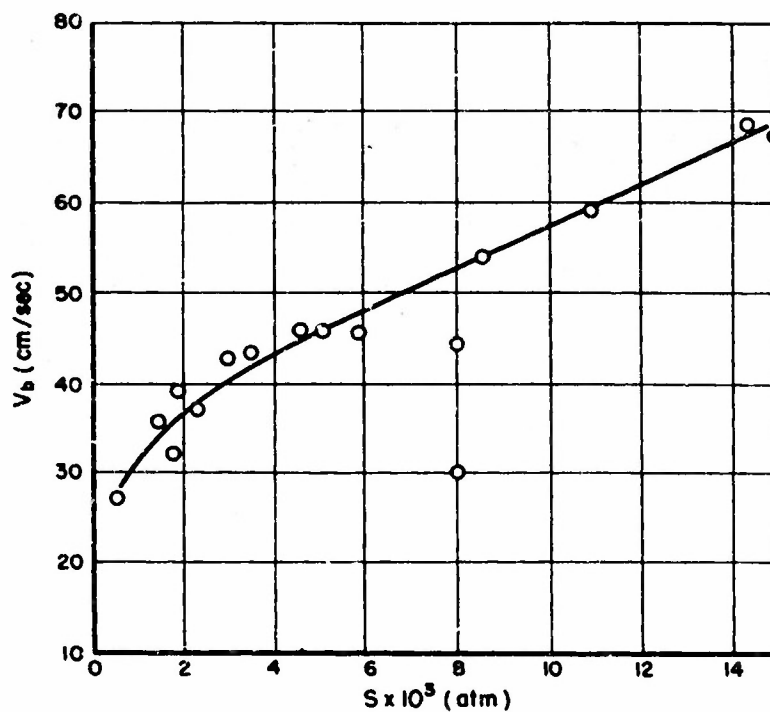by higher temperatures. Other things being equal, therefore,

Fig. 18.2-1 GRAPH TO SHOW CORRELATION BETWEEN S $(= 6.5\, p_H + p_{OH} + p_O)$
AND BURNING VELOCITY, V_b

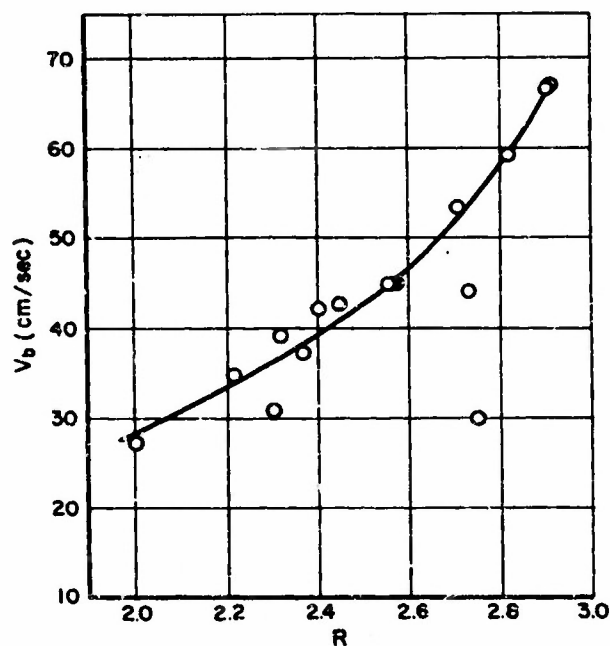Fig. 18.2-2 GRAPH TO SHOW CORRELATION BETWEEN R $(= (T_f - T_o)/(T_e - T_o))$
AND BURNING VELOCITY, V_b

- 10 -

such a correlation would be expected. As one might surmise, this situation is not uncommon in flames. In such cases the attempt to investigate the relative influence of the two mechanisms in question by these correlation techniques obviously is bound to be futile.

The importance of experiments in which one inert gas is replaced by another as a diluent in a combustible mixture has long been recognized. Consider the replacement of helium by an equal molar concentration of argon. Due to their inertness and the equality of their molar heat capacities, this exchange should not alter the thermodynamic equilibrium condition in the hot product gases. However, in view of the disparity in their masses and sizes, the transport processes should be significantly altered. This disparity is the basis of experiments which were used to test the older thermal theories. Wheatley and Linnett [40] recently investigated the application of this technique to the resolution of the question of the relative importance of heat transport and radical diffusion in flame propagation. Data on the combustion of acetylene, moist carbon monoxide, hydrogen, and methane were studied. The diluents compared were helium and argon. The ratios of the thermal conductivities, λ, and diffusion coefficients for hydrogen atoms, D_H, in the two cases were calculated in each instance and compared with the ratios of the observed burning velocities, V_b. A condensed summary of the results is given in Table 18.2-1. For the first two gases, the ratios for different proportions of fuel and diluent gases are given. In their general comments on these data the authors place less emphasis on the results for methane and hydrogen, in the former case because the method may be unreliable, and in the latter case because the original literature does not give the method used.

TABLE 18.2-1

Ratios of Burning Velocities and Transport Coefficients with Helium as the Diluent to Those with Argon as the Diluent

Gas	Ratios of			
	V_b	$\sqrt{\lambda}$	$\sqrt{D_H}$	$\sqrt{D_H}$
C_2H_2	1.61	2.69	1.30	1.68
	1.54	2.67	1.28	1.64
	1.55	2.64	1.27	1.60
CO	1.09	1.37	1.06	1.13
	1.28	1.95	1.13	1.29
H_2	2.40	1.94	1.32	1.76
CH_4	1.39	2.65	1.29	1.67

Those theories which do not give detailed consideration to the diffusion of free radicals (and thus should be classified as "thermal theories") generally predict that, other things being equal, the burning velocity should be proportional to the square root of the thermal conductivity. On this basis Table 18.2-1 should show an equality between the burning velocity ratios and the square root of the thermal conductivity ratios. The results, on the contrary, show that the thermal conductivity ratio is considerably too large in all cases except that of hydrogen. This leads Wheatley and Linnett to conclude (with reservations) that propagation of the acetylene and carbon monoxide flames cannot be by a solely thermal mechanism. They note that the conclusion (that in flames of this type, thermal conductivity is not the all important factor) was the same that Coward and Jones reached over twenty years ago.

Instead of a dependence on the square root of the thermal
conductivity, diffusional theories generally predict that the
burning velocity will be proportional to the square root of the
diffusion coefficient of the dominant radical (usually hydrogen
atoms). It is shown in Table 18.2-1 that, in contrast to the
thermal conductivities, the ratio of the square root of the dif-
fusion coefficients for hydrogen atoms is generally rather low.
While this would suggest a non-controlling influence of the dif-
fusion of hydrogen atoms, Wheatley and Linnett point out that
the diffusional theories are not so complete as the thermal
theories and the prediction is presumably more questionable.
It is interesting to note that better agreement is obtained with
the diffusion coefficient itself rather than with its square root.

While Wheatley and Linnett reach the preliminary conclu-
sion "that the flames studied are not propagated solely by the
conduction of heat ahead of the flame, and probably that the
diffusion of radicals ahead is more important than the conduc-
tion of heat," it is still questionable how much significance
should be attached to the results. The problem is illustrated
by Wheatley's and Linnett's discussion of the case of hydrogen,
in which the deviation of the thermal conductivity is apparently
reversed. The thermal conductivity ratios presented in Table
18.2-1 are calculated for the unburnt gas. It would probably
be more correct to use some mean value over the entire thickness
of the flame. In the case of hydrogen the combustion process
replaces the small, light hydrogen molecule with the larger,
more massive water molecule. Consequently, there may be very
significant changes in thermal conductivity across the flame,
and the ratio given in Table 18.2-1 may be inappropriate.
While the variations are presumably not as great in other cases,
this same type of question exists. The general point to be
stressed is, that in addition to their postulates regarding the

- 13 -

processes to be considered as controlling, both classes of theories make a number of other assumptions or approximations to simplify the mathematics. The results, therefore, can hardly be considered as the quantitative consequences of the initial postulates. An attempt to test these postulates by quantitative comparison with experimental results has questionable significance unless a real order of magnitude difference is predicted or found. After all, the problem arises largely because of the inability of these theories to predict accurately the relative size of the two factors.

The fact that the simplified approaches predict results of the same order for both factors suggests, in itself, that neither process can be neglected. It seems likely, therefore, that the relative importance of these factors will be determined largely by the chemical kinetic mechanism of the reaction involved. Very few of the flame systems studied involve reactions for which the chemical kinetics may be regarded as firmly established. In this connection it is of interest to mention a cooperative study now in progress. One of the few gas-phase reactions capable of supporting a flame for which a rather generally accepted mechanism exists is the reaction in which hydrogen and bromine combine to form hydrogen bromide [21]. Anderson and his colleagues at The University of Texas are studying this flame experimentally, while Hirschfelder and his colleagues at the University of Wisconsin are attempting to work out the theoretical picture by more detailed methods. The results of these studies will be of great interest to the field of flame propagation. Cooley and Anderson [6] reported some of their results in a recent paper. Again the burning velocity is noted to correlate with the hydrogen atom concentration but not with the bromine atom concentration.

There is a sizable amount of literature on the matter of correlation of theory and experiment. The cases treated above in some detail were chosen as illustrative examples. Correlations sometimes favor one theory slightly, sometimes the other. Both the theory and the experimental evidence must be regarded as inconclusive at this time.

Structure of Flames

A complete theoretical treatment of a flame would outline its structure in detail with respect to the distribution of temperature and concentration of reactants, intermediates, and products through the flame front. Such a detailed treatment is unfortunately not yet available. Careful photography indicates that the bright blue "inner cone" of a Bunsen burner is a thin and rather sharply demarked layer. The thickness of this luminous zone, generally of the order of 0.1 mm at atmospheric pressure, depends on the gas composition and normally varies approximately inversely as the pressure. It is commonly accepted that this zone is the seat of the major part of the chemical reaction involved in the combustion, but the smallness of the zone complicates the experimental study of its details.

Schlieren photographs reveal a somewhat sharper cone in advance of the luminous cone, and it has been suggested that the reaction takes place mainly at this surface [39]. Experiments on the vaporization of small solid particles introduced into the flames have been presented in support of this viewpoint [3]. The formation of a schlieren image depends on a gradient in optical density. The optical density would be expected to vary with changes in both the composition and density of the flame front. In most cases the effect caused by the

change in composition should be several times smaller than
that caused by the change in density. In turn, the decrease
in density is largely caused by the increase in temperature.
For these reasons, one would expect the schlieren image to
correspond very nearly to the point of maximum gradient of the
inverse of the temperature. It is certainly not obvious that
this point should also be the point of maximum reaction rate.
Klaukens and Wolfhard [20] examined this question in a study of
acetylene-air flames at low pressures (low pressures greatly
increase the thickness of the flame front). They made tempera-
ture traverses of the flames using small thermocouples and com-
pared the results with the images obtained by both schlieren
and conventional photography. As would be expected, it was
found that the schlieren image is very nearly coincident with
the maximum gradient of the inverse temperature. It was also
found that this image occurs well down in the region in which
the temperature gradient itself is easily explainable solely
by conduction from the hotter gases upstream, lying in a region
in which the temperature is still low (approximately $200^{\circ}C$), so
that no significant reaction rate could reasonably be expected.
Although the exactness of their measurements may be questioned
for a number of reasons, on general grounds these results are
more acceptable than the suggestion that the schlieren image
represents the significant reaction zone.

Friedman [11] has pointed out that the results of
Klaukens and Wolfhard must be considered tentative because of
the large correction that was necessary for radiation loss from
the thermocouple, the disturbance of the flame by the thermo-
couple, and possible interactions between the burner and the
flame front under the conditions of the experiment. By means
of a special burner, extremely fine thermocouples (beads about
0.0025 cm in diameter), and a low temperature attained by use

of very lean propane-air mixtures, Friedman believes he has reduced these errors to a negligible value. His results are shown in Fig. 18.2-3. In an analysis of the results, Friedman finds that a temperature profile below about $1100^{o}K$ can be accounted for quantitatively by thermal conduction. This again supports the viewpoint that the chemical reactions occur mainly in the neighborhood of the luminous zone rather than in that of the schlieren zone.

Using refinements of a technique which has been developed over the past several years, Fristrom, Prescott, Neumann, and Avery [12] recently made studies of the temperature profiles in propane-air flames. In this method small solid particles are introduced into a flame and their tracks photographed with the aid of intense illumination. Detailed analysis of these tracks coupled with a number of apparently reasonable assumptions allows the calculation of the temperature and velocity profile through the flame. A sample of the results is shown in the plot of the logarithm of temperature versus distance in Fig. 18.2-4. The three curves are for somewhat different compositions (ϕ = equivalence ratio). The nearly linear initial portion up to about $1100^{o}K$ (note the correspondence with Friedman) is indicative of a region of heat transport, although the authors report that the apparent thermal conductivity is larger than expected. The inflection which follows is suggestive of the onset of an endothermic process (perhaps "cracking" of the fuel). This is followed by rise to a temperature maximum and subsequent decay to an equilibrium temperature. These experiments present detail hitherto unavailable; however, the method can hardly be considered valid in spite of the care the authors have given to minimizing errors. The results cannot be compared with those obtained by Friedman because of the great difference in mixtures used. For useful comparison, it is important that conditions under both methods be as nearly identical as possible.
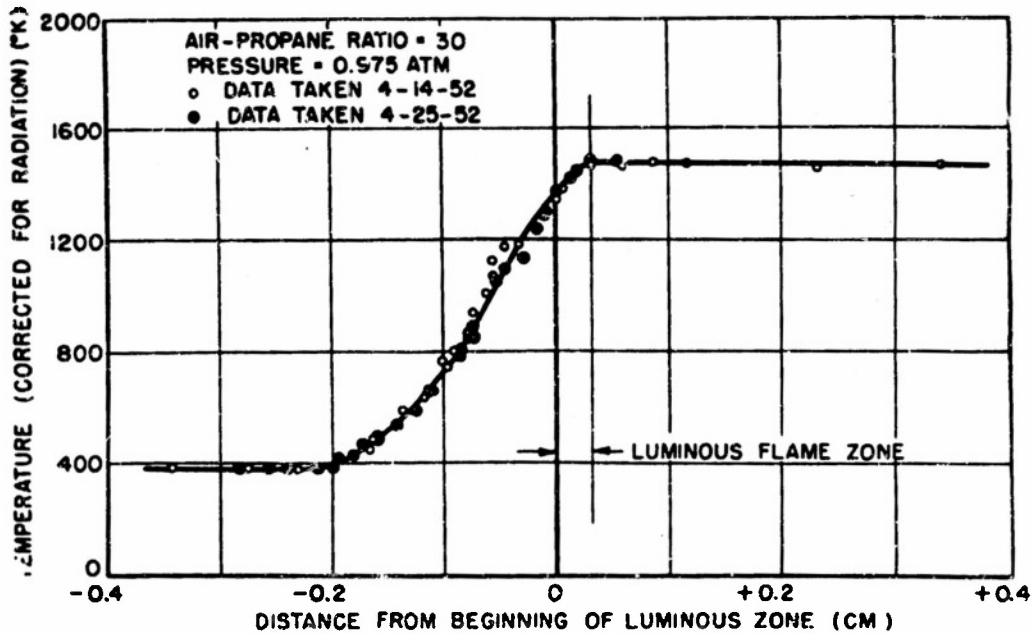
- 17 -

Fig. 18.2-3   TEMPERATURE TRAVERSE THROUGH A FLAME

The thermocouple is coated with National Bureau of Standards
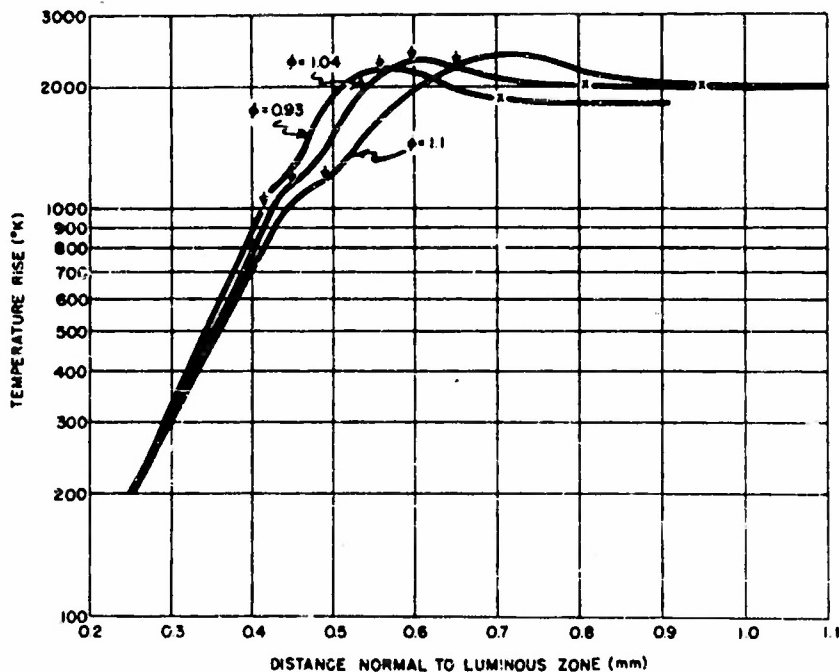ceramic coating A-418.

Fig. 18.2-4   FLAME TEMPERATURE PROFILES OF PROPANE-AIR FLAMES
WITH VARIOUS COMPOSITIONS AT ATMOSPHERIC PRESSURE

Arrows mark the limits of the luminous zones.
X marks the point fitted to the
thermodynamically calculated temperature.

- 18 -

The suggestion of an endothermic reaction to account for the initial inflection in Fig. 18.2-4 appears reasonable, but the rise to a temperature above the equilibrium value requires further explanation. The obvious suggestion in this case is that the approach to the final equilibrium involves two processes, one exothermic and fast, the other endothermic and slow. These processes might be chemical reactions; the endothermic ones, for example, being the dissociation of the combustion products; or the processes might be related to the distribution of energy among the states of the molecules (discussed in more detail later in this section), the endothermic ones being the transfer of energy to the internal modes of motion (e.g., the vibrational states of the molecules). Experimentally observed temperature peaks have been attributed to both mechanisms. The exact requirements which make such peaks occur, however, have not yet been established. Assuming thermal equilibrium among energy states, Hirschfelder and his colleagues found that their theory might allow several maxima and minima in the temperature as a function of distance, if the reaction kinetics is sufficiently complex. To date, no detailed example of this theory has been worked out.

The temperature profile and the energy profile in a flame are not necessarily simply related. The fresh gases are heated by conduction before they release any appreciable amount of chemical energy by reaction. Consequently, the total energy content will rise above the initial value. This excess energy cannot, of course, be maintained and must be conducted to provide the preheat for the next layer of gases. Thus, there exists excess energy trapped in a cycle at the flame front, being carried forward by the flow of gases and backward by conduction.

This "trapped energy" may be considered as the ignition energy for the continuous process of ignition that has been ascribed to flame propagation. Lewis and von Elbe developed this concept in terms of "excess enthalpy". Some interesting correlations based upon this concept were presented at the Fourth Combustion Symposium.

While the picture of "trapped energy" is attractive, there is a counterbalancing effect. The diffusion forward of the reactants represents a transport of chemical energy in that direction. This energy transport is in opposition to thermal conduction. The validity of the concept of energy trapped in the flame front will depend on the balance of these two transports. In an early paper, Lewis and von Elbe [22] postulated an exact compensation, and this should be the case: (a) if it is assumed that all molecules have exactly the same physical characteristics and (b) if the relation between thermal conductivity and diffusion coefficient given by simplified kinetic theory is accepted. This conclusion is an important factor in the theory of flame propagation [9] advanced by the Russian scientists Zeldovich, Frank-Kamentsky, and Semenov. However, in view of the variety of chemical species present in typical flames, the quantitative realism of these assumptions is questionable.

Several other techniques, such as line reversal and radiation brightness, have been applied to the measurement of temperatures in flames. Most of this work, however, has to do with the measurement of the flame temperature and its comparison with that expected on the basis of thermodynamics. The line reversal technique has been applied to the study of the temperature distributions in Bunsen burner flames [25] and temperatures higher than the equilibrium value have been reported, similar to the case given above. This technique does not provide information for the lower part of the temperature range (i.e., below about $1500^{\circ}K$) because of radiation weakness at low temperatures.

Also of great interest are the concentration profiles of the individual molecular species present. Much effort has been devoted to the very difficult problem of the identification of flame components by spectroscopy [13,18]. Although detailed knowledge of the spectroscopic properties of many flame components is insufficient to warrant an attempt to chart their profiles by this method, such investigations should be possible for some of the simpler molecules of which the spectra are relatively well understood (the hydroxyl radical, for example). Wolfhard and Parker recently published [42] detailed studies of diffusion flame structure, using absorption spectroscopy to obtain the concentration profiles for oxygen molecules and hydroxyl radicals. No comparable study on flames of premixed gases has been reported.

Attempts to sample a flame front for concentration-profile analysis have proved to be difficult. A satisfactory technique must be found which will allow representative samples of the reacting gases to be obtained without appreciably disturbing the flame. This technique must keep the sample representative as it is transported to the analytical equipment. In spite of the difficulties involved, several approaches are being pursued with slow but encouraging progress [10]. There should be interesting developments in this field during the next few years.

Another kind of "structure" in flames is the distribution of molecules among their energy states rather than in space. Under conditions of thermal equilibrium the energy states will be populated according to the laws of quantum statistics and the temperature will be properly defined in terms of the modulus of the distribution. Thermal equilibrium is normally maintained by the exchange of energy during molecular collisions. The question then arises as to whether the redistribution of the energy, so rapidly released in combustion, is fast enough to establish thermal equilibrium everywhere in a flame.

Since the intensity of spectral lines depends on the populations of the states involved, spectroscopy is a natural tool for investigation of this question. In addition to dependence on state population, line intensity depends on the probability of transitions between states, so that this technique is limited to the study of the distribution of energy for simple molecules whose quantum-mechanical and spectroscopic properties are reasonably well known. Furthermore, the technique is limited to study of the distribution of energy among the "internal" modes of motion, since these, rather than the translational modes, are involved in the spectral emission. This field of investigation is quite active [4,14,34], and the results may be broken into three general classes. In the first class, the distribution among the states, whether they be in the rotational, vibrational, or electronic modes of motion, seems to obey the statistical laws with a single unique temperature. This agrees with thermodynamic predictions. In the second class, the distribution appears to be statistical in each mode (i.e., rotational, vibrational, and electronic) but with independent "temperatures" for the three modes. The disparity between these temperatures is generally greatest near the reaction zone, disappearing downstream as would be expected. The third class (mostly observed at low pressures) consists of cases in which one or more of the modes of motion does not appear to be in equilibrium within itself. For such a mode a temperature, even in the limited sense used above, cannot be defined.

Spectroscopic studies of energy distribution are very important to the general understanding of the processes of energy transfer, and the difficulties which they suggest to the understanding of flames is evident. For example, the customary use of equations of the Arrhenius form to represent the dependence of reaction rates on temperature might well be

in jeopardy in some cases. The extent of such deviations from
thermal equilibrium is still unknown, however, and whether they
are vital or incidental to the over-all process of flame propa-
gation is still an open question.

Space Burning

In large-scale practical burners, conditions are gener-
ally much more involved than in the case of the simpler flames
used in the study of the mechanism of flame propagation. Mixing
of fuel and air may not be complete, resulting in an inhomoge-
neous combustion region. In addition, the flow is generally
highly turbulent and vortiginous, as contrasted to the rather
regular flow of the simpler burner. These conditions raise
the question of the influence of flow irregularities on flame
propagation.

In recent years the subject of flame propagation in turbu-
lent gases [26] has been given increasing attention, largely be-
cause of the development of jet engines and gas turbines. Al-
though conditions in actual engines are generally much too com-
plicated for fundamental study of the problems involved, it has
been possible to make pertinent studies by construction of
simpler experimental burners. Results obtained with the latter
are then compared with the over-all performance characteristics
of the former.

It has been suggested that the nature of the influence
of turbulence on flame propagation will depend on the relative
sizes of the scale of turbulence and the normal thickness of
the flame zone under nonturbulent conditions. If the scale of
turbulence is small compared with the flame thickness, its in-
fluence will be manifested mainly through increase of the ther-
mal conductivity and diffusion coefficients so important to

flame propagation. On the other hand, if the scale of turbulence is large compared with the flame thickness, turbulence will distort the flame surface and increase its area substantially. Then, even with the normal burning velocity, the larger surface permits a greater rate of fuel consumption and thus leads to an apparent large increase in burning velocity. Very few cases of small-scale turbulence in flames actually exist. Even if the initial stream is prepared in a manner so as to provide an example of small-scale turbulence, the turbulence subsequently generated by the heat release of the flame itself seems to be sufficient to transform the situation into a case of large-scale turbulence.

Crude theories based on the concept of mere distortion of the flame front by turbulence have shown only limited correlation with experimental data. Better results are obtained by assuming that the flame front is carried forward by turbulent eddies, so that the actual burning velocity is the sum of the normal burning velocity and the velocity of displacement of the wave by turbulent motion.

Visual observation and ordinary photography (long exposure) show gross similarity between the flames burning at the end of a burner tube under laminar and turbulent conditions. The familiar sharp luminous zone of the laminar case is replaced by a thicker, diffuse, and somewhat brushlike zone in the turbulent case. Significance has been attached to this "smeared-out" appearance of the reaction zone, but more careful photography indicates that it is illusory. In high-speed schlieren photographs the flame has the appearance of an undulent, convoluted surface. The "smearing-out" ordinarily observed is due to the time exposure of this moving surface. This surface is illustrated by the photographs in Fig. 18.2-5 which are taken from the work of Karlovitz [19]. Such observations provide the basis of the concepts of the effect of large-scale turbulence.
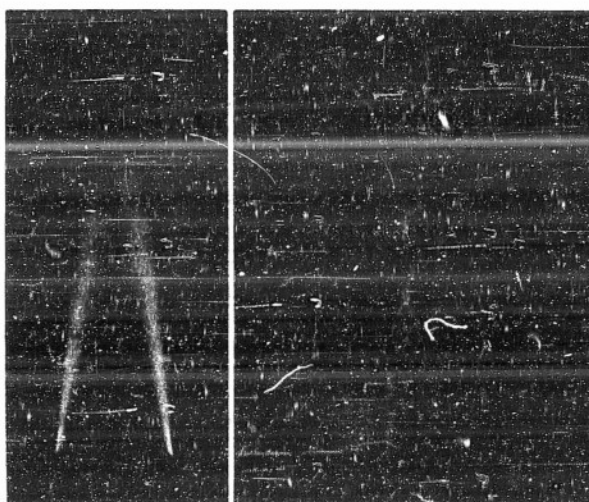
Fig. 18.2-5

In burners more closely modeling the combustion chambers
of jet engines, where the velocity of gas flow may be very high
(up to 300 ft/sec or more in a ramjet), the turbulence and vor-
ticity become much more pronounced, and the concept of a single,
continuous burning surface begins to stretch the imagination.
While it may be that the combustion consists of the normal propa-
gation of a number of flame surfaces into the unburnt gases, it
is a question whether the thermal conduction and diffusion,
characteristic of that process, are not greatly augmented or
perhaps overshadowed by a more or less gross macroscopic mixing
of the burnt and unburnt gases. If this is the case, the carry-
over of the normal flame speed as a characteristic of the propa-
gation would not seem warranted. More attention should be fo-
cused on the space-wise rate of heat release by combustion.
The rate of release of heat per unit volume would be limited
by the rate of mixing or by the rate of the chemical reaction,
whichever is slower.

In this model, the limits imposed by the mixing require-
ments are rather difficult to handle in any simple manner.
However, the limits imposed by the chemical reaction rate, when
it is the controlling factor, are more amenable to detailed
formulation [1,28]. Mixing burnt gas with unburnt gas increases
the rate of heat release by virtue of the increased rate of re-
action due to the higher temperature. At the same time, dilu-
tion of the reactants by the products produces an opposite ef-
fect. For this reason there should be an optimum value for the
mixing. For simple reactions, calculation of this optimum is
an elementary problem. With reasonable values for the various
parameters it is easy to show that the optimum generally occurs
when the greater portion of the mixture (for example, eighty
per cent) is burnt gas. The maximum heat release per unit vol-
ume so calculated is many times greater than that prevailing in

ordinary combustion chambers (although perhaps only several
times greater than that of the most efficient of the high heat
release jet engines operating at ordinary pressures). This
suggests that the rate of mixing is the controlling process
and that improvements in the volumetric efficiency of combustors should be sought along these lines. There may, of c..rse,
be regions in a combustor, such as at flameholders, where the
mixing is fast enough for the chemical kinetics to be controlling.

Reduction in the pressure of a combustion chamber would
be expected to increase the rate of mixing but to decrease markedly the rate of the chemical reaction. This may usually be considered to be approximately a second-order kinetic process.
Thus, at low pressures limitation of rate of heat release by
the chemical kinetics becomes a distinct possibility. For combustors that must operate over a range of pressures it may well
be that the efficiency on a volume basis will be limited at one
extreme by the mixing rate and at the other by the chemical rate.
In such cases, improvement of mixing may accomplish little since
the low pressure regime may require a combustor of much greater
volume than those used at high pressures.

It should be possible to calculate the minimum volume
required to bring about a given rate of heat release, provided
sufficient chemical kinetic and thermal data are available for
the system in question. This calculation then, would provide
a partial answer to the question of volume requirement. However,
accurate kinetic data are not now available for these calculations. The limitations on the mixing rates which can be attained
with reasonable pressure drops and heat losses in the combustion
chamber are not yet clear. To complicate the problem, in the
case of chain reactions (which include most combustion reactions)
one must consider the loss during the mixing of chain-carrying
radicals and products.

No attempt has been made to go into detail in this
section because the subject is in a state of flux. However,
the study of flame propagation is essential in designing high-
ly efficient combustors that are so important to the continued
development of jet engines. Steady improvement in the under-
standing of combustion in highly turbulent gas streams may be
expected, and a valid theory of flame propagation should emerge
from the concepts outlined above or from new and more satisfac-
tory viewpoints.

18.3 FLAME STABILITY

Stabilization

Anyone who has had to deal with an occasional balky
Bunsen burner is aware that the localization of flame at a
desired position is not always easy to achieve; the burning
sometimes occurs noisily in the tube, sometimes irregularly
above the burner, and sometimes not at all. Flame stabiliza-
tion deals with the processes involved in providing a localized
and steady combustion zone.

Flame propagation may be considered as a process of con-
tinuous ignition. The objective in flame stabilization, then,
is to bring about this ignition at the desired position in the
burner. This stabilization is generally achieved by establish-
ing a local interference with the normal processes of flow or
of flame propagation. The interference may be provided by such
factors as admixture of additional gases, variation in flow
velocity, creation of flow irregularities by means of obstacles,
addition or subtraction of heat, or removal of active chemical
species by surfaces (quenching). The importance of each factor
is determined by the particular conditions; therefore, flame
stabilization in Bunsen burners, lifted flames, and high velo-
city combustion chambers are discussed separately.

The Bunsen burner, consisting of a jet of combustible
air-fuel mixture flowing out of a tube, is an instructive ex-
ample of the problem of stabilization. The question about such
flames is why they stay in position. Of course, if the gas
velocity is too high, the flame will not anchor and will be
blown away, or if it is too low the flame will enter into the
tube and move to a different point of attachment. But between
these two limits there exists a considerable range of flow ve-
locity over which the flame will remain on the burner rim.

The condition for stability is that a flame front will find a stable position if the local burning velocity equals the local gas velocity somewhere in the mixture but nowhere exceeds it.

In a flame of truly uniform gas velocity, stability would occur only when the flow velocity was equal to the flame speed. However, flow in tubes, whether laminar or turbulent, does not have a uniform velocity profile. Near the wall the velocity of flow approaches zero. Consequently, if the flame speed were unaffected by the tube, flashback could always be expected. This does not occur because the wall and the flame zone usually interact so that the wall is both a heat sink and a quenching surface for the chemical reactions. Both effects influence the detailed heat and material distribution in the reaction zone, and the burning velocity approaches zero at the wall. This reduction of both gas velocity and flame speed at the surface makes possible local matching of the two.

Lewis and von Elbe [24] have studied flashback in detail, and their results indicate that the tube radius, R, and the critical rate of gas flow for flashback, V, should be correlated through the critical velocity gradient at the wall, g_F (for a parabolic velocity contour, $4V/\pi R^3$). Figure 18.3-1, taken from their work, illustrates this correlation. There is no quantitative work available to check the relative importance of a surface in reducing chain carriers and gas temperature. The problem is complicated in that the heat flow into the wall may also be partly returned to the boundary layer of the gas, raising its temperature above normal.

Although the flashback point is relatively well understood, the situation is more complex regarding the stable region and the blow-off point. Here the interaction between the combustible stream and the atmosphere is important.
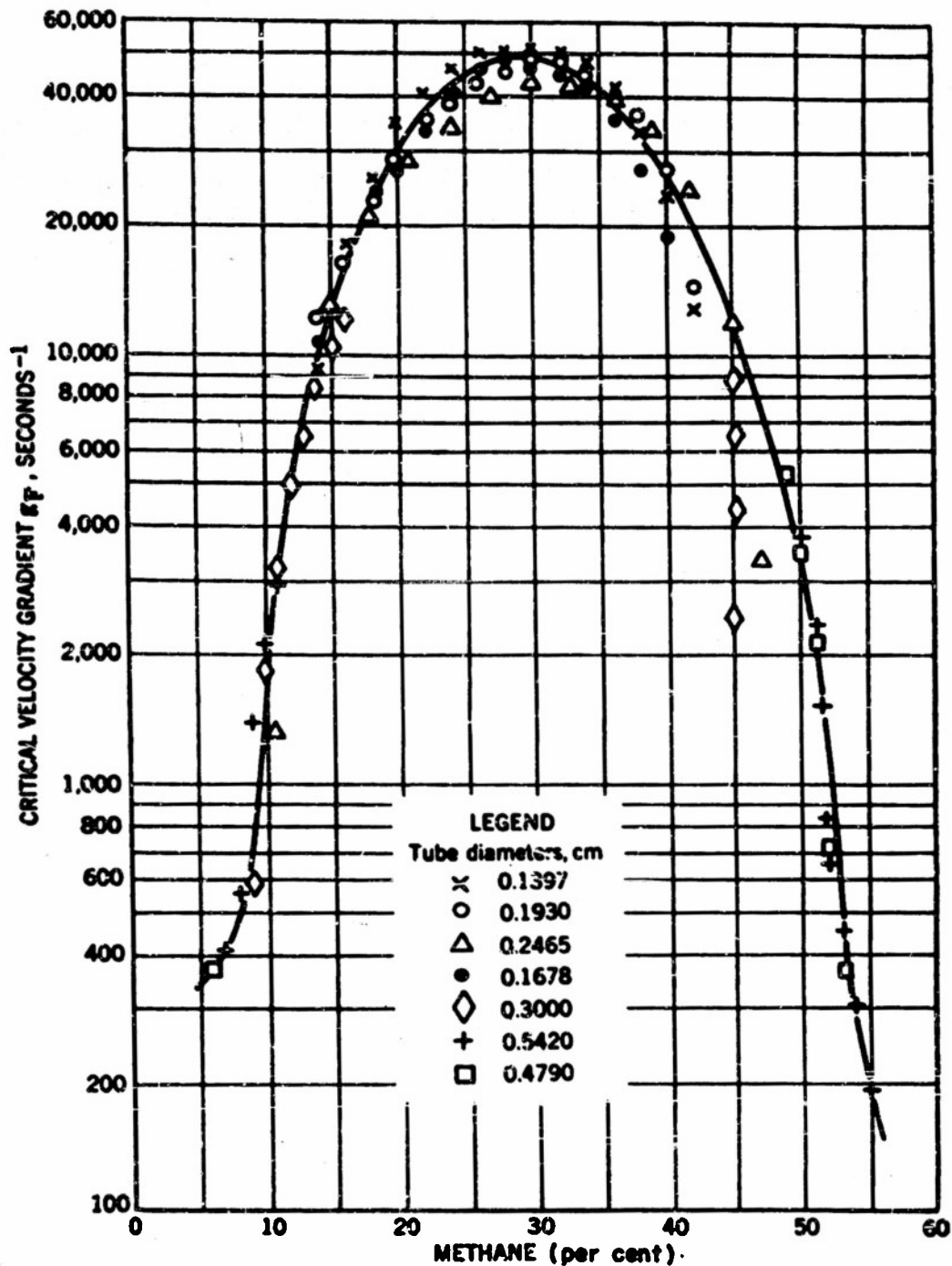
Fig. 18.3-1 CRITICAL BOUNDARY VELOCITY GRADIENTS, g_F,
FOR FLASH-BACK IN CYLINDRICAL TUBES OF DIFFERENT DIAMETERS

The methane is mixed with oxygen at room temperature
and atmospheric pressure.

- 31 --

This interaction causes changes in velocity and concentration
not encountered at the flashback point. The effect of these
combined changes is that the flame and flow-velocity profiles
vary with distance above the burner rim. As the flow velocity
is increased above the critical flashback velocity, the flame
zone will move to a new equilibrium position farther from the
rim, where the local burning velocity is influenced less by the
presence of the solid wall and can, therefore, counterbalance
the higher flow velocity. The combined effects of the atmos-
phere and the burner wall are difficult to formulate precisely.
However, if tube diameter is the only variable, the correlation
in terms of a critical velocity gradient holds even into the
turbulent flow regime [41]. It would obviously be desirable to
understand in more detail the interaction of the jet with the
atmosphere so that velocity and composition profiles could be
predicted and their influence calculated. The influence of
the surrounding atmosphere on the blow-off point is shown in
Fig. 18.3-2, taken from the original paper [23] of Lewis and
von Elbe on stability of burner flames.

The need for a better understanding of the aerodynamic
aspects of the flow is shown by the difficulty of predicting
the occurrence of "lifted" flames. This phenomenon may occur
in both laminar and turbulent streams, but particularly in the
latter. It is characterized by flames stabilized far away from
the nozzle exit in the mixing zones between a fuel-rich jet and
an oxygen-containing atmosphere. There is no wall influence to
account for adjustment to stable position. The lifted flame is
stabilized entirely by variations in burning velocity and jet
velocity.

Turbojet and particularly ramjet engines require the
liberation of heat in combustible streams moving at high velo-
cities (100 to 600 ft/sec). Consequently, one of the most im-
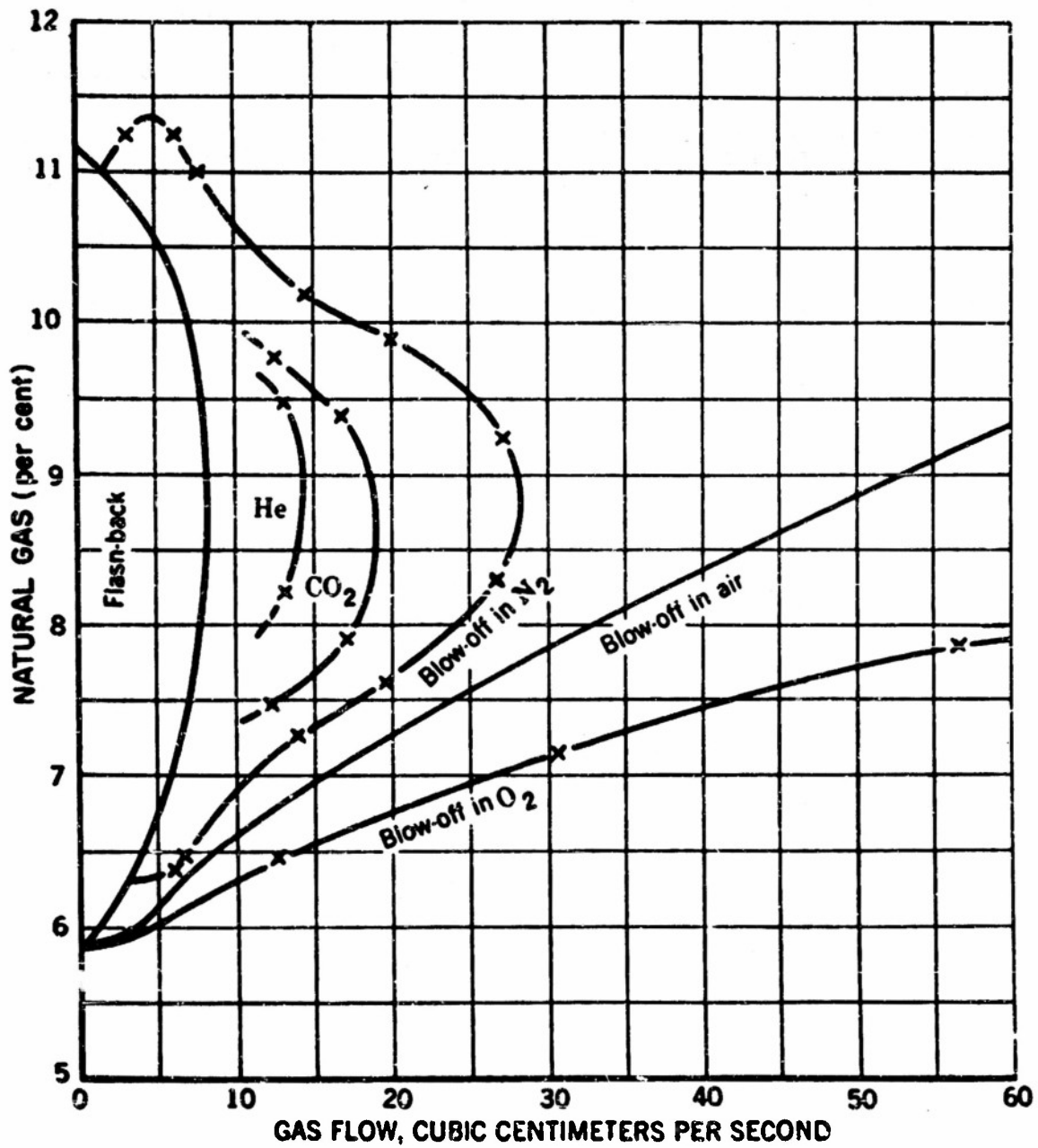portant present-day fields in combustion research deals with

Fig. 18.3-2 EFFECT OF NATURE OF SURROUNDING ATMOSPHERE ON
BLOW-OFF OF NATURAL GAS-AIR FLAMES FROM
CYLINDRICAL BURNER TUBE WITH DIAMETER OF 0.577 cm

the stabilization of flames in such streams. The mechanisms discussed so far are inadequate for operation at such high velocities without blow-off. With the high velocity gradients encountered, no matching of burning and jet velocities is possible; however, the normal transport of energy into the unburnt gases may be augmented. This augmentation may be achieved either by a feed-back mechanism, whereby a portion of the hot burnt gas is recirculated and used in the ignition of fresh combustible, or by the use of separate energy sources such as electrical sparks and hot pilot jets.

Experiments on the spark ignition of a quiescent gas have shown that a critical-discharge energy exists above which a combustion wave will propagate and below which it will die out. If similar experiments are carried out in a moving stream, somewhat higher values of the critical energy are required, even though the disturbing influence of the electrodes has been reduced. If sparks of sufficient energy are discharged through a flowing gas at frequent enough intervals, a stabilized flame may be simulated. Such a method of stabilization is qualitatively different from any of those previously described. The initiated flame, swept away continuously from the ignition point, continues to spread as it moves with the stream.

The critical energy requirements for the hot gas kernel to propagate cannot as yet be predicted with precision. Furthermore, the high-speed pictures of Olsen, Edmonson, and Gayhart [32] indicate quite clearly that the rate of flame propagation is not uniform but is markedly slowed down in the early stages of kernel expansion. A particularly complex balance exists in which unsteady flow is linked with temperature and concentration gradients. No detailed description of all the phenomena appears possible although plausible models may well be established.

Stabilization may be obtained by means of hot jets. The combustible mixture is injected into a separate stream of heated gas. Provided the ignition requirements are met, a flame will stabilize in the mixing zone between the jets and continue to propagate into the combustible stream. Temperature, velocity ratio, and turbulence level are the principal variables determining whether a propagating flame will form. The subsequent rate of flame propagation is sensitive to the initial condition set up by two annular streams.

An aerodynamically induced feed-back of hot gas may be used as a means of stabilizing flames at high flow velocities. A gross steady-state flow reversal regime is established behind blunt air foils or baffles mounted at right angles to the stream direction. At sufficiently high flow velocities a bluff structure will give rise to eddies in its wake, where sufficient time for occurrence of exothermic chemical reactions is provided. Blow-off occurs at a particular critical velocity which is highest for mixtures of high flame speed, and the stability regime increases with increased baffle dimensions and ambient pressure.

The theory of stabilization by baffles is in an early stage of development. It is generally assumed that a stable vortex system or mixing zone exists behind the stabilizer. Unburnt mixture is continuously introduced into this vortex where reaction takes place. All energy released in the vortex is considered to be used to heat a portion of the main stream, producing ignition by a thermal mechanism. As the flow velocity of the stream increases, the energy requirements for ignition increase. Flame propagation ceases when the heat dissipated by the vortex is insufficient to ignite the main stream. It is difficult to formulate a precise description of this energy requirement, but by a number of simplifying assumptions the composition of the unburnt mixture can be correctly related

to the blow-off velocity, pressure, and baffle dimensions for particular experimental systems. The generality of such correlations is not yet established, and the theory is too incomplete to allow accurate or sure prediction.

In addition to their effect on energy requirements, the operating conditions also affect the rate of heat production by the vortex system. In some cases, at least, it appears that the limitation by chemical reaction rate (discussed in the preceding section) applies. The kinetics of the crucial chemical step is probably second order, and the mixing in the critical zone where stability is achieved is so rapid that the reaction may be uniform. Under these conditions there exists an optimum mixture that provides the maximum rate of energy release. A change in operating conditions may reduce this rate below maximum. Pressure is also a factor determining the maximum rate of heat release from a mixture.

It is easily seen that flame stabilization in high velocity-streams is far from understood. However, continued research is beginning to provide an understanding of the interrelation of the variables involved, and attempts to explain the parts played by chemical kinetics and transport processes are showing encouraging progress. There is little doubt that such studies will ultimately provide a more scientific and systematic basis for the design of jet engines.

Instabilities

The instabilities known as flashback and blow-off were considered under the heading of stabilization. In this section. a different class of instabilities which might be termed "pathological" are discussed.

About a hundred years ago the beautiful experiments of Tyndall on "singing flames" were the forerunners of many other instances in which remarkable instabilities are found in flame systems. The advent of jet engines has centered interest on oscillations and flow instabilities.

Flow oscillations may be triggered spontaneously by small disturbances (as in singing flames), or they may be the result of programmed operations (pulsed fuel flow, for example). In either case the oscillations are accompanied by variations in position and shape of the flame front. Pressure waves are generated, and the general flow pattern of the system changes periodically.

These fluctuations are of great interest, from both fundamental and practical points of view. The designer of engines, for example, must be aware of such disturbances since the accompanying pressure and velocity fluctuations will profoundly affect heat transfer rates, combustion limits, and performance efficiencies of many essential components, and may bring about structural failures. In view of the difficulty of predicting the onset and magnitude of the instabilities, it is, at present, customary to avoid operational conditions where they are likely to occur. However, it is entirely possible that significant engineering progress might be made by judicious use of flow oscillations.

One of the simple cases of instability will be considered first. If a combustible mixture in a cylindrical tube, closed at one end, is ignited at the open end, a flame front will travel into the tube. Vibrations will often occur as the flame reaches certain positions in the tube, with frequency and amplitude depending on the position of the flame front. In Fig. 18.3-3, taken from the pioneering work of Coward [7], is shown a continuous photograph of the flame front as a function of time recorded on a revolving-drum camera. Time runs from right to left.
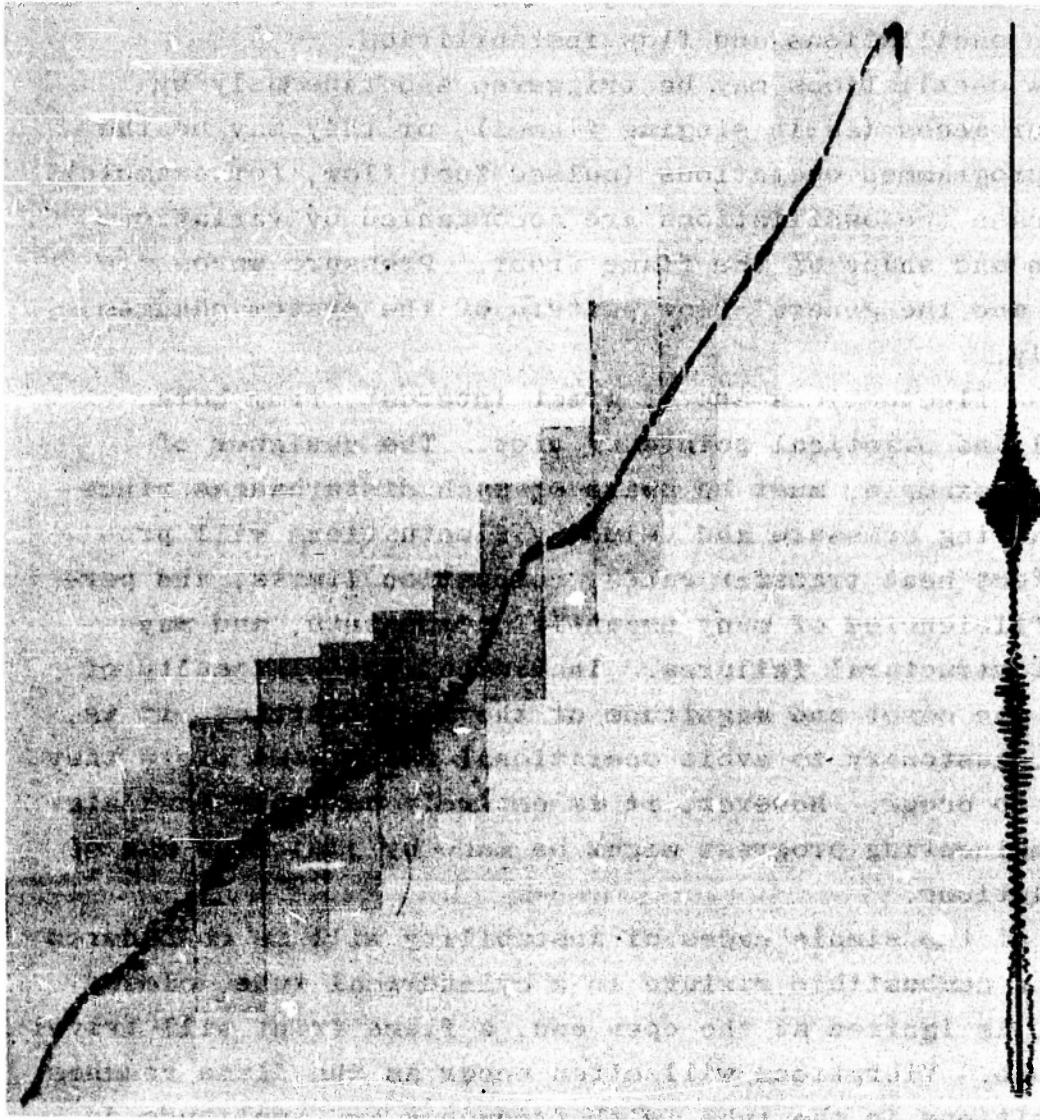
Fig. 18.3-3 COMPOSITE DRUM CAMERA RECORD OF FLAME PROPAGATION
IN A TUBE CONTAINING A 10-PER CENT METHANE-AIR MIXTURE

The flame moves from bottom to top.
The top trace is the luminous flame front;
the bottom trace is the corresponding
pressure fluctuation.

The regions of oscillation are clearly discernible, and the accompanying pressure fluctuations are shown at the bottom of the figure. Since tube diameter has little effect on the observed frequencies and doubling of tube length halves the frequencies, there is little doubt that this oscillation is a longitudinal resonance effect. An acoustical analysis of the problem predicts the occurrence of standing waves and the shift in frequency as the flame front moves through the tube. Of course, such an analysis must take into account, as one of its principal arguments, that the velocity of sound and other acoustical properties of the duct change with the temperature of the gas column.

Although the simple acoustic model adequately predicts which frequencies may be expected, it does not predict the harmonic which will predominate or the amplitude of the oscillations. The general conclusion from Coward's work was that the various phases of the vibrating period tend to develop between antinode and node of one of the possible modes of resonance, their amplitudes rising to a maximum and falling away. No clue is given to the means by which oscillations are started and maintained.

In many cases, photographs indicate that oscillations are coupled with large changes in flame-front area. Since the rate of heat addition is a function of flame-front area, burning velocity, and combustion efficiency, any or all of these factors may be responsible for maintained oscillation in the flame.

There are many other possible interactions between the flame and its environment which can give rise to stable or quasi-stable oscillations. An instructive case is the interaction between the fuel supply and the combustion process.

If a rise in pressure in the combustion tube is reflected as a decrease in fuel flow, a complete "feed-back loop" may be set up. A similar situation can occur if the rate of gas generation on the surface of a propellant is a function of pressure. These kinds of interaction have been recognized in actual engines, but the theoretical prediction of their occurrence and of the amplitude of the effect is unsatisfactory at present. As previously noted, changes in flame-front area may be closely coupled with oscillations in flames. The work of Markstein [30] illustrates that single smooth flame fronts may degenerate into unusual cellular structures as shown in Fig. 18.3-4. This cellular structure occurs most readily with fuels of high molecular weight on the rich side of stoichiometric burning from a large burner. Addition of methane suppresses the tendency for cell formation and shifts the onset to even richer mixtures, finally preventing cell formation entirely. Shallow cells are sometimes observed with methane alone, but here the onset is on the lean side. Markstein observes that mixtures giving rise to cellular structures have a greatly enhanced tendency for the excitation of organ-pipe oscillations in the tube in which they are formed.
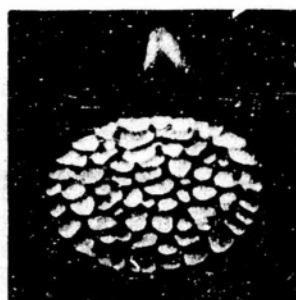
The dependence of the cellular flame phenomenon on the molecular weight of the fuel suggests that preferential diffusion of the fuel and oxygen is very important in these flames. Considerable evidence is accumulating which indicates that wherever nonplanar combustion waves exist the composition of the mixture entering the reaction zone is altered by diffusion, leading to large variations in the remaining unburnt gas. These diffusional changes can be very large and may explain a variety of apparently unrelated observations. One of the earliest examples is the propagation of flames in very dilute hydrogen-oxygen mixtures [5]. Flames can propagate in mixtures where
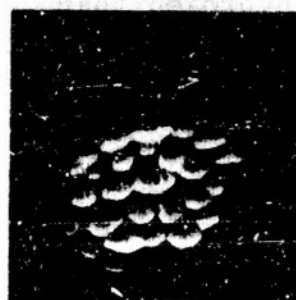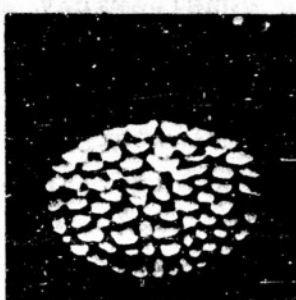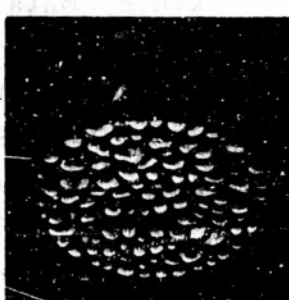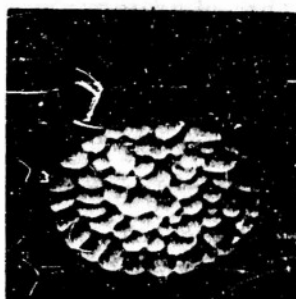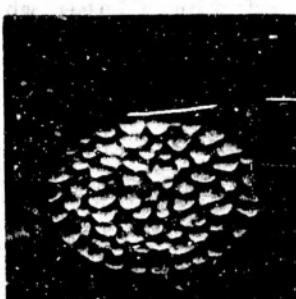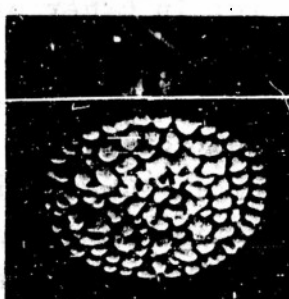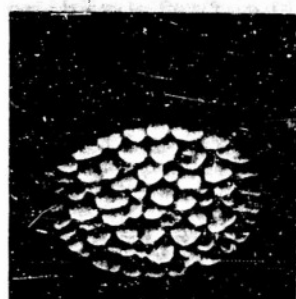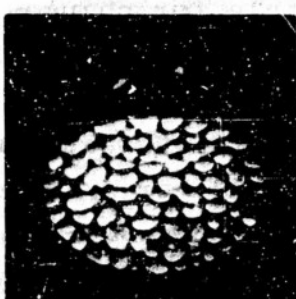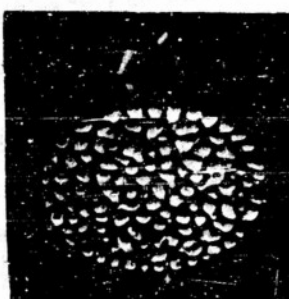
Fig. 18.3-4 CELLULAR STRUCTURE OCCURRING IN
SINGLE SMOOTH FLAME FRONTS

the temperature rise would be only a few hundred degrees after burning if there were no change in composition. Careful observation indicates, however, that flame propagation does not proceed through a continuous combustion wave. The flame front breaks up into a number of cells. Hydrogen diffuses rapidly toward the reaction zone, and the combustion actually takes place in a mixture containing considerably more hydrogen than indicated by the initial composition.

Similar changes in composition apparently account for various phenomena in Bunsen flames near their tips. Preferential diffusion of reactants to the tip can cause appreciable concentration changes. These changes are often so profound that they give rise to quite different reaction products. Soot, for example, will form where the diffusional changes are large but not in other parts of the flame where the changes are small.

Diffusion effects may also be responsible for observations on spark ignition energy requirements for the ignition of combustible mixtures. The minimum ignition energy as a function of mixture composition occurs either on the lean or rich side of the stoichiometric point depending on the molecular weight of the fuel. It may well be that diffusion into the initially sharply curved flame front is again responsible for changes in the fuel-oxidizer ratio.

One of the most startling examples of nonrepetitive types of instability is found in materials that can detonate. If a gas column of hydrogen and oxygen, or a solid or liquid explosive, is ignited and the combustion process is documented, using high-speed techniques, an initially slow flame may be observed to veer off into a reaction proceeding at a much higher rate, possibly several thousand times faster. It has long been recognized that the flow equations describing heat addition to a stream have a

solution in the supersonic regime in addition to the more familiar subsonic one. The fact that an oxygen-acetylene mixture, for example, can be burned or detonated, depending on the experimental situation, shows that both processes can be realized in practice. It is, however, the transition from the one propagation rate to the other that attracts our interest.

Although the equations for the steady-state reactions can be handled in simple cases for both burning and detonation, at present it is not possible to predict the transition from one case to the other. There is also no method known for determining whether an exothermic reaction will proceed by combustion or by detonation. The influence of boundary conditions such as charge size and initiation energy are apparently vital to the determination of the course of the reaction.

There is much discussion in the technical literature about the nature of knock in internal combustion engines. Persistent controversy as to whether the end gas actually detonates or merely reacts rapidly throughout its entire volume seems to be settled in favor of detonation. The arguments against detonation--that it cannot be induced in a hydrocarbon-air mixture in a tube or that antiknocks are not inhibitors in systems which can detonate in a tube--have little validity since preflame reactions in the end gas undoubtedly take place. Therefore, a system entirely different from the original fuel-air mixture is involved. Recent ultra-high-speed pictures [29,31] indicate the existence of shock waves by the presence of discontinuities moving at supersonic speed. It is not surprising, in view of the complex shape of combustion chambers and the complexity of the gas movements, that the observed detonation fronts are not readily visible.

There now exists an overwhelming body of evidence, from both spectroscopic studies and actual sampling and chemical analysis, that profound chemical changes occur in the gas mixture

before combustion has engulfed the entire charge. During the
compression by the piston and the further pressure rise caused
by the expansion of the charge that has reacted, organic perox-
ides and formaldehyde form in appreciable quantities in the end
gas and are often accompanied by a blue chemiluminescent glow.
A careful analysis has been made by Walsh and others [8] of the
chemical reactions proceeding in the end gas with a variety of
fuels. They conclude that the preflame reactions in the end gas
control the occurrence of knock. These reactions are of a chain
type taking place in the gas phase and not at the wall. The phe-
nomena in engines are found to be similar to those observed in
ignition studies outside of engines, usually at lower pressures
and temperatures, where the occurrence of a two-stage ignition
process has often been observed [38]. The first phase of this
process includes peroxide formation during the initial attack
of oxygen on the hydrocarbon molecule. The action of pro- or
antiknocks in influencing the speed of this first phase is the
key to their effectiveness. Detailed understanding of these
reactions may provide clues to better agents or at least indi-
cate what further possibilities exist for controlling knock.

18.4 CONCLUSION

The Scientific American of July 1952 quotes as follows
from its columns of July 1852:

> "What do we know of flame excepting this:
> 'It is the exhibition of a certain action
> of certain substances, such as carbon,
> hydrogen, and oxygen.' We are in the dark,
> yet, respecting one of the most common and
> simple chemical phenomena."

This statement may also aptly describe the situation one
hundred years later. It is hoped, however, that in this chapter
it has been made clear what information is still to be sought.
This perhaps, is what one means by progress.

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